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Durable Copper Polyimide Adhesive Bonds

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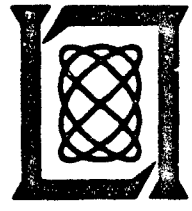

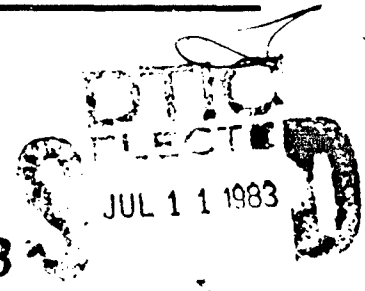

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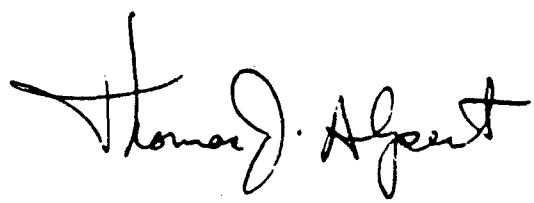

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DURABLE COPPER POLYIMIDE ADHESIVE BONDS

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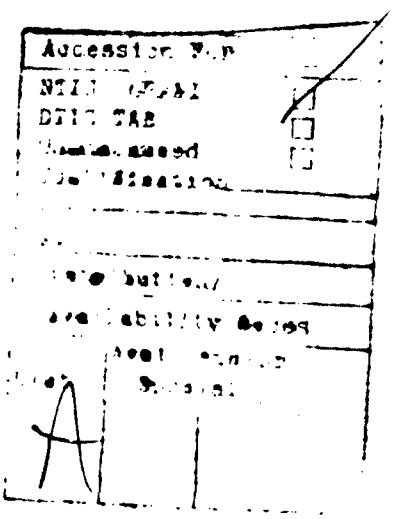
ABSTRACT

With an optimum chemically converted surface on copper, durable structural adhesive bonds can be produced. By this particular alkaline oxidizing formulation and post-sealing, excellent structural bonds, which are both thermally and chemically stable, are achieved. The stability of these oxidized surfaces has been demonstrated through extensive tensile lap shear, interlaminar shear testing, and verifying peel tests.

Although bonding has been primarily evaluated with a polyimide adhesive, the effect of the hot alkaline oxidizing solution on epoxy fiberglass substrates was explored using the ASTM interlaminar shear bending test and electrical resistance comb pattern.

Quantitative analytical procedures for constituents in the alkaline oxidizing bath are described.



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1.0 INTRODUCTION

Successful adhesive bonding to copper is a critical step in the printed circuit process. Not only must the bond be structurally and thermally durable to withstand the heat from today's electronic components and vapor-phase soldering, it must also resist the attack by subsequent processing chemicals. In this report, tensile lap shear tests on a particular alkaline oxide formulation called Red Oxide are discussed (1,2). Thermal tests were conducted at and following exposure to a high temperature of 204°C (400°F). Excellent thermally resistant adhesive bonds were measured. In order to improve chemical durability, the copper oxide surface is sealed in a manner analogous to aluminum anodizing sealing. This has proven to be a significant step in improving its chemical stability.

2.0 LAP SHEAR TENSILE TEST RESULTS

Peel tests for quality control predominate in the printed wiring industry primarily for reasons of simplicity and economy. However, this test does not offer specific results which indicate failure trends nor is peeling the exclusive mode of adhesive failure.

In the structural adhesive category, particularly with aluminum, lap shear testing prevails. Yet even here there is controversy. As shown by Guess (3), however, thin tensile lap shears are informative if the same adhesive is used throughout the tests. Consequently, the adhesive polyimide resin, Kermid 601(2), was used throughout our test. The impregnation is done by Oak Co. of New Hampshire using a style-#108 glass cloth carrier. The lap shear test specimen consisted of a 1/2-in. bonded overlap of two 1-in. x 4-in. x 1/16-in. electroplated Cu plates essentially consistent with the ASTM procedure(4).

The reason why copper requires a conversion coating was described at least forty years ago by Campbell and Thomas, when they showed that copper almost instantaneously developed a "tarnish" of cuprous oxide(5). The test value in Table I shows "tarnished" copper from the 200^{o}C press heat cure. The tarnish is rapidly formed and it is nonadherent as evident from the 700 psi result.

TABLE I

THIN LAP SHEAR RESULTS

Process	Tensile Lap Shear (psi)
Cu (tarnisned)	700 ± 65
Black Oxide E	1200 ± 95
Black Oxide R	1170 ± 90
Black Oxide C	1825 ± 200
Alkaline Permanganate (1%)*	1300 to 1700
Red Oxide	2300 ± 80
Red Oxide (Sealed in H_2O)	2590 ± 100

*H. N. Vazarini, "Surface Preparation of Cu and its Alloys for Adhesive Bonding and Organic Coatings," J. Adhesion, Vol. I (July 1969) P. 208.

Three commercially available copper treatment solutions Black Oxide E, R and C were evaluated and those conclusions were previously reported (6). Those results as shown in Table I were all inferior to the Red Oxide process as presented by Raytheon in an Air Force supported program(1), and earlier by Damary(2).

The recommended modified Red Oxide process is shown in Table II. This report will discuss the results that have led to these recommendations.

TABLE II

SUMMARY OF THE RED OXIDE PROCESS

NOTE: Between each processing step, thorough water rinsing is essential.

1. PRE-ETCH

   42 Be' ferric chloride solution (39%)
   with HCl acid (Hunts chemical etch)
   Time: 1 minute at room temperature

2. ACID DIP

   25% HCl for 1 minute

3. RED OXIDE SOLUTION	MAKE UP (gm/l)	ANALYZE (gm/l)
Sodium chlorite (80% pure)	37.5	30
Sodium hydroxide	6	5
Trisodium phosphate (12 H_2O)	25.3	10

   Temperature: 85 to 90°C
   Time: 2 minutes

4. SEAL BY BOILING IN H_2O FOR 15 MINUTES

5. BAKE 2 HRS. @ 110°C

6. PRESS BONDING OF POLYIMIDE FILM ADHESIVE

   Hot press at 205°C (400°F)
   Time: 90 minutes
   Pressure: 350 psi
   Cool: 90 minutes under pressure to 60°C (140°F)

3.0 THE RED OXIDE PROCESS

3.1 Pre-etch

Hennemann and Brockman(7) have shown the importance of "surface morphology and its influence on (Al) adhesion." Tensile shear test results have verified that with a copper etch of ferric chloride and hydrochloric acid, a 10% improvement in adhesion is achieved. This correlation between surface morphology and bondability is only true if the adhesive is able, after wetting the surface, to invade the oxide morphology. Unfortunately the polyimide has a high processing temperature and probably does not flow easily as a lower melting epoxy into the interces of the etched structure. The contours for the various surface states can be seen in the scanning electron microscope (SEM) photos of Fig. 1.

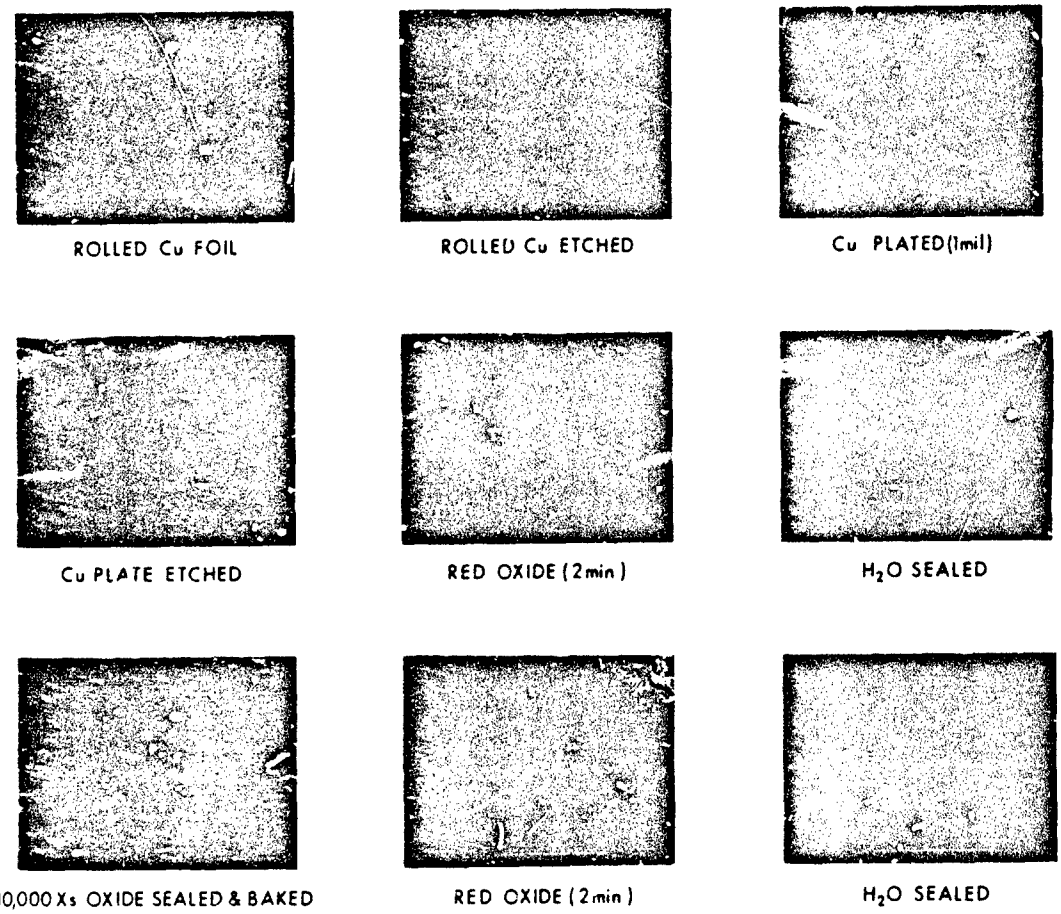

Fig. 1. Scanning electron microscope photographs of Cu Red Oxide surfaces.

NOTE: The final magnification can be calculated by measuring the size of the 10U bar in each photo.

In Fig. 1, the first view shows the rolling marks of the 4-mil Cu foil used for sampling. After etching, the grain pattern of the Cu can be seen, and the rolling lines of the presses have disappeared. The third view shows rolled Cu foil unetched but electroplated with one mil of non-additive copper sulfate using periodic reverse. The grain structure is quite large and distinctive. The etch removed about 1/2 mil of this deposit and shows the epitaxial growth of the plated Cu on the grain pattern of the rolled copper foil.

The SEM scans of Red Oxide boiled and unboiled surfaces are shown. Although the boiled surface gave stronger bond strengths, they are optically similar. At 10,000 X magnification approximately one-nanometer holes are evident in the oxide surfaces.

3.2 Alkaline Oxidation

The formulation of the hot alkaline oxidation bath is shown in Table II. On initial make-up, the bath was inadvertently weighed out as shown under the "Analyze" column. When subsequently analyzed, the results were approximately 20% lower than expected. This was due to the sodium chlorite being only 80% pure; the "Make-up" column therefore shows the adjusted quantity needed to achieve the 30 g/l composition. Similarly, the commercially available trisodium phosphate has 12 waters of hydration. That has been compensated for, as shown in Table II.

The effect on adhesion of each ingredient in the alkaline oxidizing solution is shown in Fig. 2. Chlorite alone at 95°C for three minutes produced lap shear values of about 1250 psi. With the trisodium phosphate added to the chlorite solution the values increased by 500 psi to 1750 psi. When the caustic soda completed the bath, the lap shear values were a consistent 2300 psi. Sealing by hot-water oxidation produced lap shear values over 2500 psi. This treatment was introduced primarily as a chemical sealant, and is more fully described later in this report.

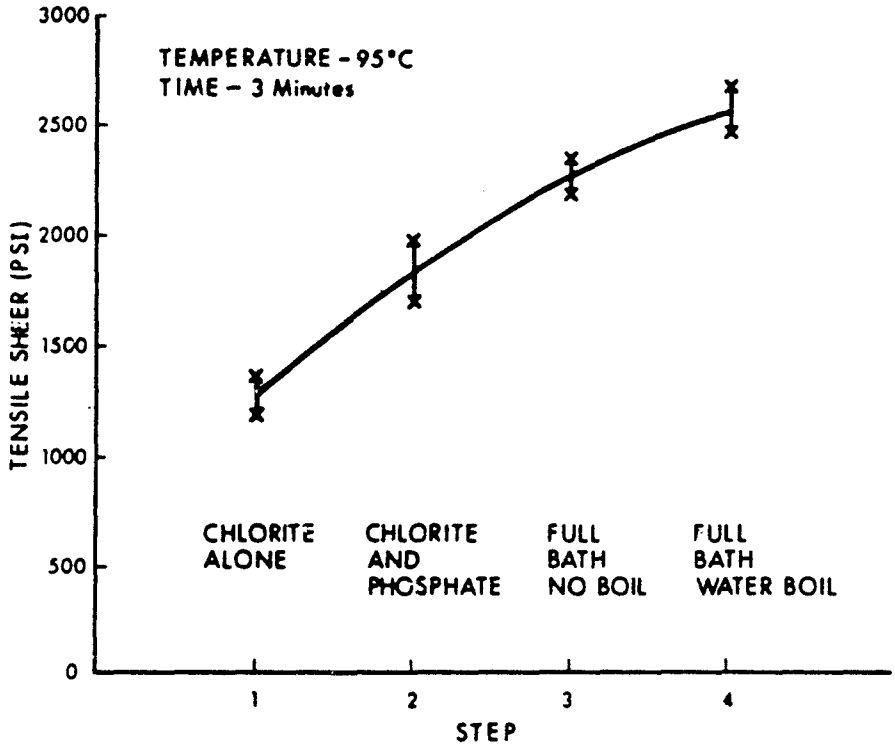

Fig. 2 Red Oxide solution vs. lap shear.

A word of caution to the experimentor in evaluating these highly alkaline solutions: DO NOT USE GLASS BEAKERS. Within eight hours the silicon from the silicate will appear in the oxide coating, jeopardizing the characteristics of the adherend layer, and yielding adhesive values 50% lower than expected.

The effect of the hot alkaline solution on G-10 (epoxy fiberglass) was suspect. However, no physical degradation occurred after as long as ten minutes' immersion, as verified by the ASTM-D-1002-72 Interlaminar Shear Test. Electrical insulation characteristics were similarly unaffected.

3.3 The Effect of Temperature

In Table III, the effect of varying the solution's temperature vs. tensile strength is shown. Although the solution is relatively insensitive to temperature variations, it appears that temperatures higher than 90°C are detrimental using a 3-minute dip time. An optimum of 85°C is recommended.

TABLE III

EFFECT OF SOLUTION TEMPERATURES

(Time: 3 minutes)

Solution Temperature °C (°F)	Tensile Lap Shear psi	Average Deviation	Percent
82 (180)	2285	40	2
85 (185)	2285	75	3
90 (195)	2190	30	1
96 (205)	2045	110	5

3.4 Solution Stability

As much as 30 square feet of copper surface can be processed through a liter of the oxidizing solution without adhesion values decreasing (see Fig. 3). These duplicate runs were conducted prior to introduction of the water-sealing operation.

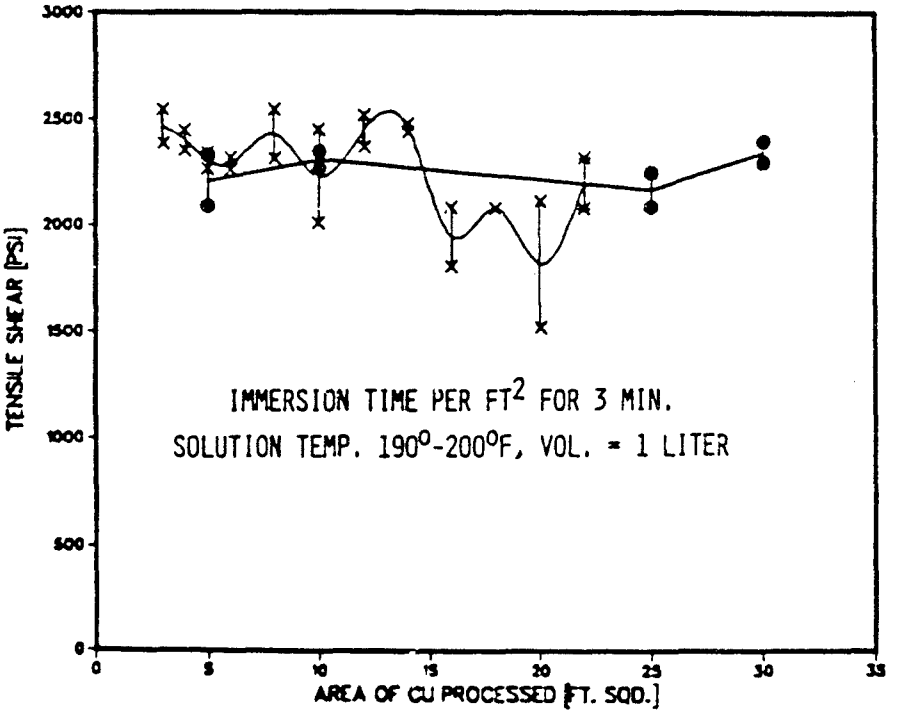

Fig. 3. Red Oxide solution stability vs. area Cu processed.

While the 30 square feet of Cu was processed, chemical analyses were conducted on the solution. In the final analysis the caustic soda was down 33%, the chlorite down 20%, and the phosphate down only 8%. Although there was this decrease in chemical makeup, the adhesion values did not reflect this consumption.

4.0 CHEMICAL ANALYSIS

In the Appendix, the details of the computer-aided chemical analysis are provided. The concentration of the trisodium phosphate and sodium hydroxide was determined by potentiometric method. The solution is titrated with standard hydrochloric acid to two end points while monitoring the changes in pH.

The concentration of $NaClO_2$ was determined by adding potassium iodide (KI) and sulfuric acid (H_2SO_4) to a known quantity of solution and titrating with a standard sodium thiosulfate ($Na_2S_2O_3$) solution. Analysis of $NaClO_2$ in a standard sample solution of Red Oxide gave accurate and precise determination to within $\pm$2.5 percent. Unfortunately, this method is used also for the determination of Cu (I) and Cu (II). However, since the concentration of copper in solution found by atomic absorption is less than 25 mg/l, the effect on determining the concentraton of $NaClO_2$ is negligible, and is therefore neglected (see Appendix).

Although the tensile lap shear values did not decrease as copper was processed, the bath composition did change. The concentration changes of the three chemicals are detailed in Table IV.

TABLE IV

CHEMICAL CONCENTRATION CHANGES PER AMOUNT OF COPPER PROCESSED

Sq. Ft. of Processed Cu (3 min.)	NaClO (g/l)[2]	NaOH (g/l)	Na_3PO (g/l)[4]
5	31.4	7.2	6.1
10	28.6	7.1	5.8
20	24.3	5.4	5.9
30	21.0	4.3	5.6

In Fig. 4, the normalized concentration changes are shown as copper is being processed. With this kind of data, additions to the bath can be made as printed circuit boards are being processed by keeping track of the amount of copper surface passed through the solution.

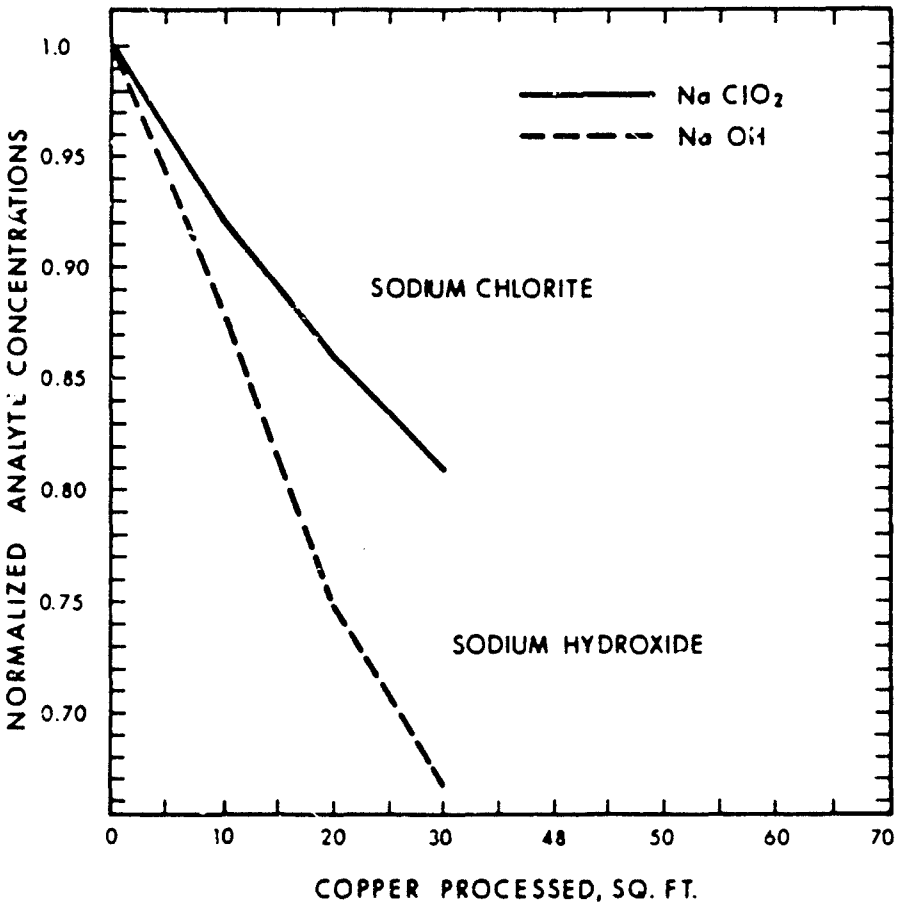

Fig. 4. Depletion of bath ingredients, concentrations normalized.

5.0 THERMAL LAP SHEAR TEST RESULTS

One of the reasons polyimide rather than an epoxy is preferred, is its excellent durability and strength at high temperatures. To verify this feature, tensile lap shears were conducted at 204°C, as well as after the test specimen had been soaked for eight hours at 204°C. These results in Table V show no adverse effects on bond strength after exposure to several hours of 200°C temperature.

TABLE V

THERMAL LAP SHEAR TEST RESULTS

Standard Red Oxide Process + 8 Hours @ 204° C
Tested @ 25°C = 2150 psi
Tested @ 204°C = 2190 psi

6.0 INTERLAMINAR SHEAR TEST RESULTS

Practically all the tests supporting the conclusions of this report are based on the lap shear test results. Recently McDevitt & Baun(8) recommended using a short beam test, as shown in Fig. 5, for evaluating an adhesive bond. The test is normally used to measure the interlaminar adhesion of reinforced composites. G-10 epoxy fiberglass has interlaminar shear values of 6000 psi. Our optimum results exceeded 10,000 psi. The test specimen is small (1 in. x ½ in. x ¼ in.). Brass plates approximately 4 inches square were Cu electroplated, processed by the standard Red Oxide method, and bonded as per Table II. The small test specimens were machined from this larger plate.

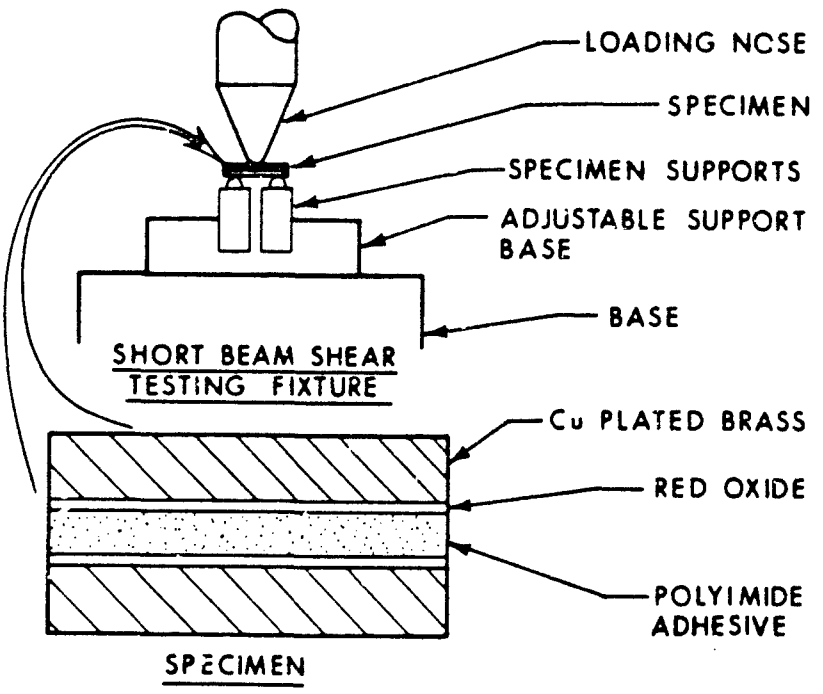

Fig. 5. Illustration of short beam test geometry.

The tests were informative (see Fig. 6) and showed that the 2-minute immersion in the Red Oxide solution was superior to 3 minutes. The post-cure of the 2-minute immersion specimens at 200°C indicated a significant thermal durability. However, there were indications that the post cure is not needed.

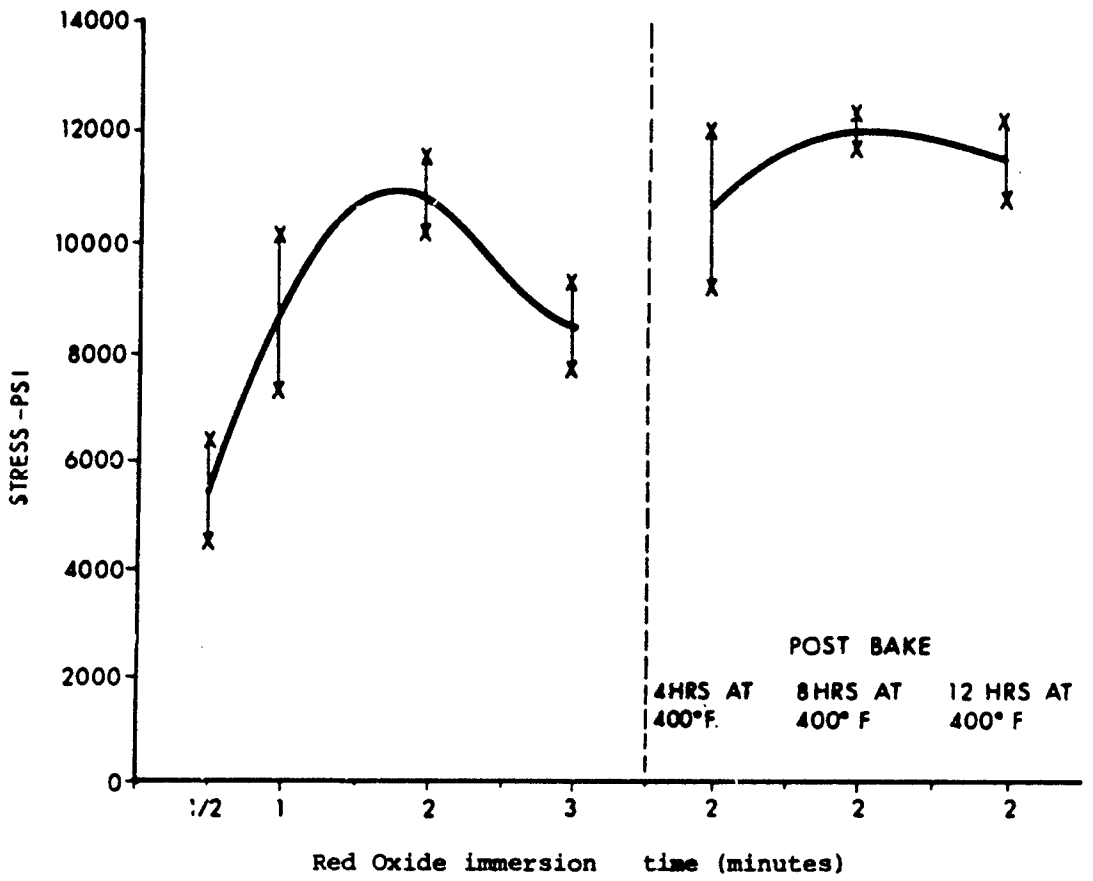

Fig. 6. Interlaminar shear copper/PI bond test.

The post-bake portion of the curve indicates that the adhesive bond tolerates eight hours of post-baking at 200°C, but that after such exposure there is a downward trend. If the circuitry is to be exposed to additional high temperatures during its processing, then it is recommended that the post-cure be omitted. Additional laminations and vapor-phase soldering (215°C) would produce additional post-curing. From these results, there would be no concern about the bond integrity due to thermal exposure of 200°C.

7.0 PINK-RING PHENOMENON

In a review article(9) on multilayer printed-circuit problems, reference is made to the "chemical attack along the inner layers on the black oxide". In the printed-circuit industry vernacular, this is often referred to as "pink ring". When the phenomenon is viewed normal to the surface, the diffusion of chemical from the metallizing process shows a uniform lateral penetration into the oxide/imide interface of as much as 100 micrometers (see Fig. 7).

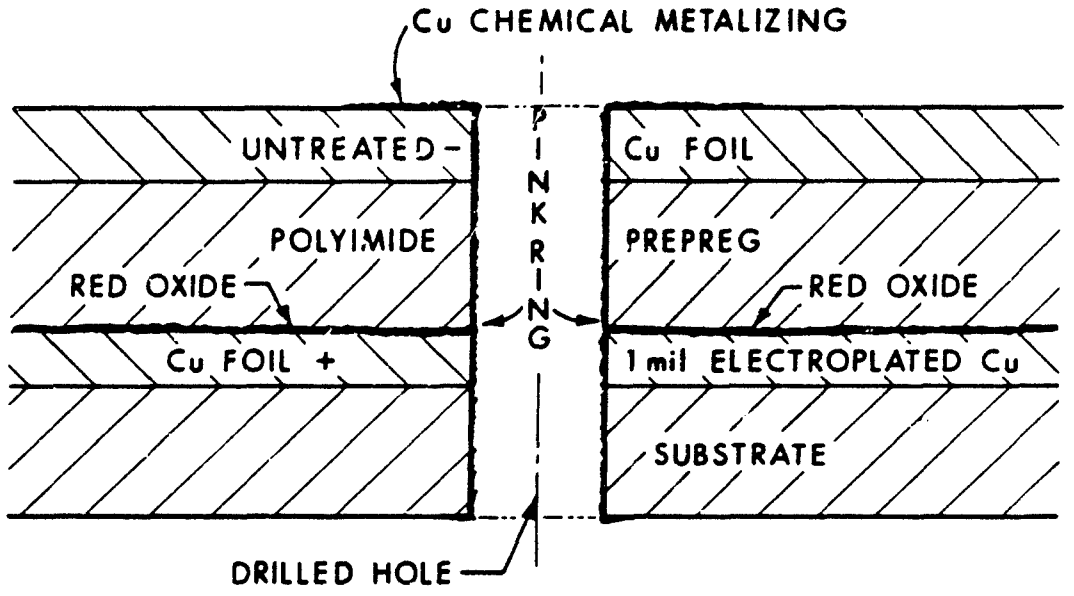

Fig. 7. Pink Ring.

Without post-sealing with boiling water, the plain Red Oxide processed parts were quite susceptible to pink ring. It appears that this boiling-water step is analogous to the sealing of anodically formed aluminum oxide that becomes hydrated and sealed by boiling in water. There may also be a second effect of leaching any residual alkali that might be locked in the interces of the etched copper oxide surface that could inhibit adhesive cure. The boiling in water also enhances the mechanical adhesion values as shown in Figs. 2 and 6.

8.0 THE NATURE OF THE OXIDE LAYER

For over twenty years, there have been articles on the nature of the oxidized copper(10). One of the more recent was by Siominski and Landau(11). They referenced Bickerman's text on adhesion and state that the outer surface is primarily cupric oxide, and that there is a gradient through the thickness that becomes progressively richer in cuprous oxide. Further, they state that cuprous is an unstable form and may be oxidized to cupric oxide during high-temperature pressing by reacting with residual oxygen, water, or various decomposition products. The function of the oxide coating is to act as a barrier and to prevent the reaction of copper with the adhesive (otherwise the adhesion would be jeopardized by a weak boundary layer).

X-ray analysis of the oxides gave evidence of both cuprous and cupric oxide on the surface. At least within the first 100 angstroms of the top layer the Red Oxide forms cupric oxide, as can be seen from the data plotted in Fig. 8. The ratio of copper to oxygen as determined by Auger analysis shows that the upper bonding surface is cupric oxide. Since both oxidation states of copper are present, it is assumed the bottom surface is cuprous rich.

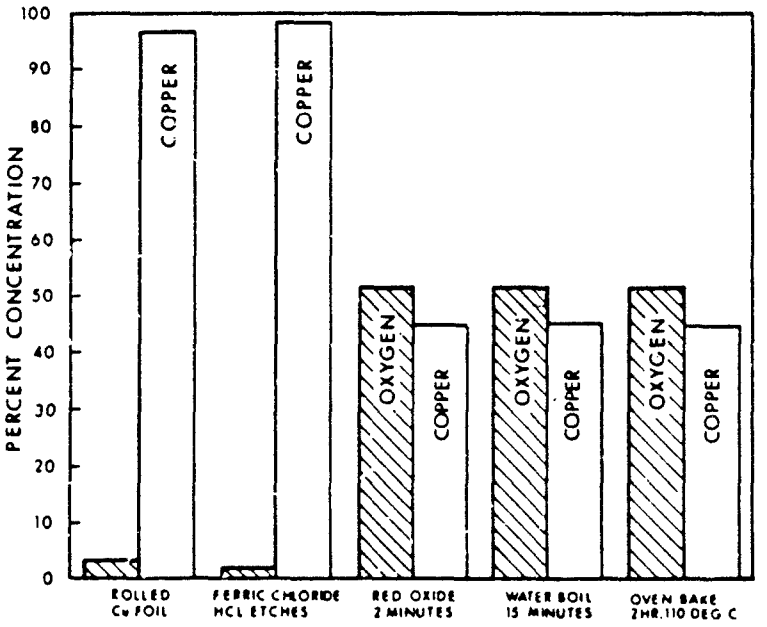

Fig. 8. Percent concentrations of oxygen and copper.

9.0 CONCLUSION

The Red Oxide process provides a stable mechanical and thermal adherend Cu surface for adhesive bonding, especially in multilayer PI circuit applications.

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APPENDIX

1.0 ANALYSIS OF SODIUM CHLORITE ($NaClO_2$)

The stoichiometric chemical equations used are symbolic statements of the quantitative relation between the reactants and the reaction products. Eq. 1 represents the conversion of KI to iodine, and Eq. 2 the reaction of free iodine with standard $Na_2S_2O_3$. This indirect reaction is used to compute quantitatively the concentration of $NaClO_2$. End points are found by color changes of the solution during titration.

$$NaClO_2 + 4KI + 2H_2O \longrightarrow 2I_2 + NaCl + 2K_2SO_4 + 2H_2O \quad (1)$$

$$2Na_2S_2O_3 + 2I_2 \longrightarrow Na_2S_4O_6 + 2NaI \quad (2)$$

The concentration of $NaClO_2$ in gram/liter =

$$\frac{(\text{Normality of } Na_2S_2O_3)\ (\text{Vol. } Na_2S_2O_3)(90.44 \text{ grams/mole of } NaClO_2)}{4(\text{Vol. } NaClO_2 \text{ titrated})}$$

2.0 POTENTIOMETRIC METHOD FOR THE DETERMINATION OF Na_3PO_4 AND NaOH

The solution is titrated with standard HCl solution to two end points which are indicated by a change in the pH values (pH = the negative log of hydrogen ion concentration). A computer generated curve is plotted of pH vs. the volume of HCl (see Fig. A1) Showing those 2 end points.

The first derivative of the curve is shown in Figure A2.

The first end point corresponds to the following combined reactions:

$$NaOH + HCl \longrightarrow NaCl + H_2O \quad (3)$$

$$Na_3PO_4 + HCl \longrightarrow Na_2HPO_4 + NaCl \quad (4)$$

By adding equations 3 and 4 the result is:

$$NaOH + Na_3PO_4 + 2HCl \longrightarrow 2NaCl + Na_2HPO_4 + H_2O \qquad (5)$$

The first end point is the molarity of the mixture of NaOH and Na_3PO_4.

The second end point is represented by the equation:

$$2HCl + Na_2HPO_4 \longrightarrow 2NaCl + NaH_2PO_4 \qquad (6)$$

The difference between the first and second end point is the conversion of dibasic to the monobasic phosphate. Every molecule of trisodium will produce a molecule of di or monobasic phosphate which will go to phosphoric acid (H_3PO_4) with further titration. A knowledge of these concentrations is essential to the computation of NaOH, Na_3PO_4, or NaH_2PO_4.

Method to calculate the concentrations of NaOH and Na_3PO_4 in Red Oxide solution:

a. End point No. 2 minus end point No. 1 = ml of HCl to titrate the Na_2HPO_4 in equation 5.

b. $\frac{\text{ml of HCl in step a (normality (N) of HCl)}}{\text{ml of sample titrated}}$ = N of Na_2HPO_4

c. $\frac{\text{N of } Na_2HPO_4}{2}$ = Molarity (M) of Na_3PO_4 in bath

d. (M of Na_3PO_4) (163.94 grams Na_3PO_4/mole) = g/l Na_3PO_4

e. $\frac{\text{(end point No. 1) (N of HCl)}}{\text{ml of sample titrated}}$ = M of mixture of NaOH + Na_3PO_4

f. M of mixture - M of Na_3PO_4 in (c) = M of NaOH

g. (M of NaOH) (39.9978 grams NaOH/mole) = g/l NaOH

(N = Normality, M = Molarity)

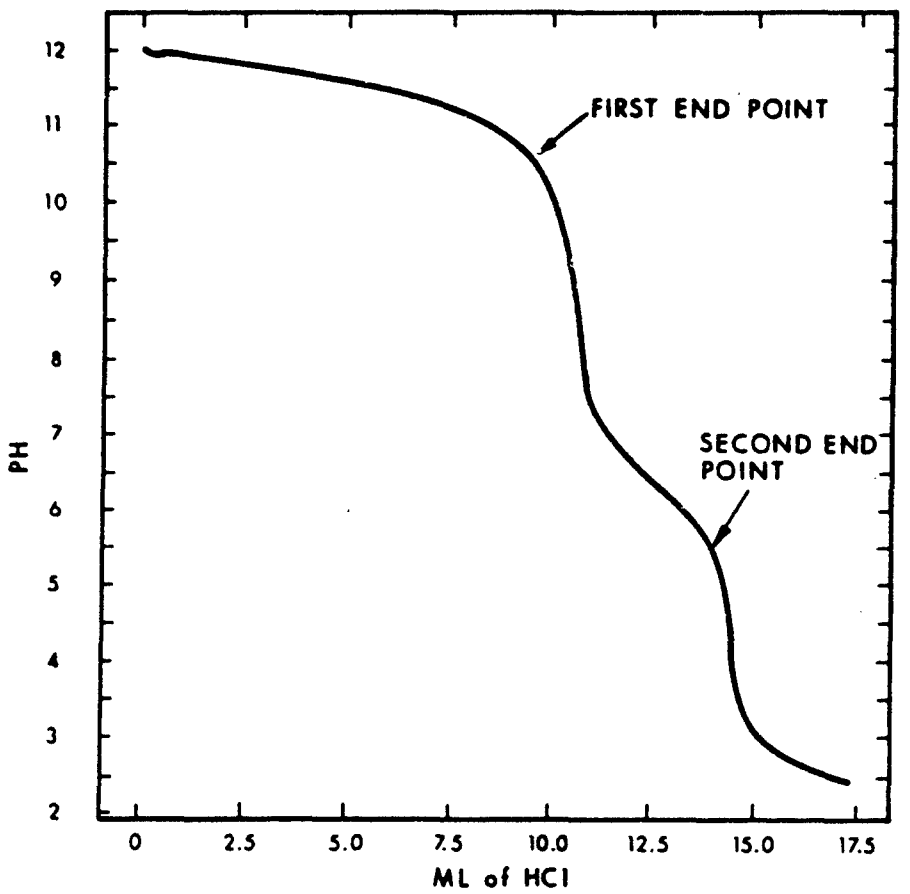

Fig. A1. Red Oxide solution titration

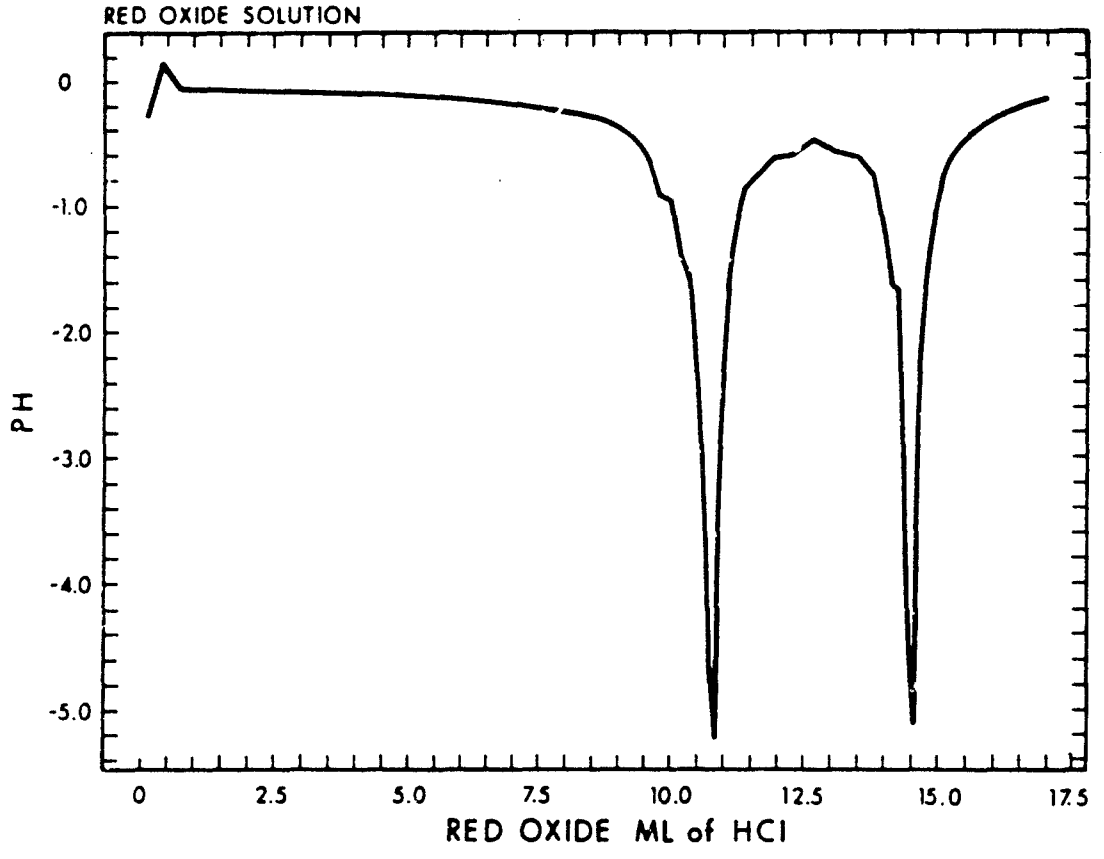

Fig. A2. First and second end points from plotting first derivative

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analytical procedures
polyimide adhesive
copper adhesive bonds
copper oxide

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

With an optimum chemically converted surface on copper, durable structural adhesive bonds can be produced. By this particular alkaline oxidizing formulation and post-sealing, excellent structural bonds, which are both thermally and chemically stable, are achieved. The stability of these oxidized surfaces has been demonstrated through extensive tensile lap shear, interlaminar shear testing, and verifying peel tests.

Although bonding has been primarily evaluated with a polyimide adhesive, the effect of the hot alkaline oxidizing solution on epoxy fiberglass substrates was explored using the ASTM interlaminar shear bending test and electrical resistance comb pattern.

Quantitative analytical procedures for constituents in the alkaline oxidizing bath are described.

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